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(54) Title: ZINC BORATE			
(57) Abstract Zinc borate compositions having a ZnO:B ₂ O ₃ ratio of 4:1. The hydrated zinc borate 4ZnO·B ₂ O ₃ ·H ₂ O and anhydrous zinc borate 4ZnO·B ₂ O ₃ are especially useful as fire-retardants and smoke-suppressant additives for polymeric compositions.			

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ZINC BORATE

This invention relates to improved zinc borate compositions, and more particularly, this invention provides a new hydrated zinc borate having
5 a high dehydration temperature which offers significant advantages for compounding with plastics and rubbers at elevated temperatures. The anhydrous form of the zinc borate is also provided, offering advantages for compounding at even higher
10 temperatures.

Background of the Invention

Many different hydrated zinc borates are known and several find commercial application as fire retardants and smoke suppressants for various
15 polymers. Hydrated zinc borates are also used as anti-corrosive pigments for coatings and have demonstrated fungistatic and bacteriostatic properties which find many applications.

The known hydrated zinc borates include

$\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$, $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3.5\text{H}_2\text{O}$, $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot7\text{H}_2\text{O}$,
3 $\text{ZnO}\cdot5\text{B}_2\text{O}_3\cdot14\text{H}_2\text{O}$. (sometimes designated
 $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot9\text{H}_2\text{O}$), $\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot2\text{H}_2\text{O}$, $\text{ZnO}\cdot5\text{B}_2\text{O}_3\cdot4.5\text{H}_2\text{O}$,
5 $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3\text{H}_2\text{O}$, and $6\text{ZnO}\cdot5\text{B}_2\text{O}_3\cdot3\text{H}_2\text{O}$. See Supplement
to Mellor's Comprehensive Treatise on Inorganic and
Theoretical Chemistry, Vol. V, Part A, Pages 577-578,
Longman Group Ltd (1980). See also pages 572-6 for a
review of anhydrous zinc borates. Several of these
10 zinc borate hydrates have commercial importance,
especially as fire retardants and smoke suppressants
for polymers, rubbers and coatings. The relatively
high dehydration temperature (about 290°C) of
 $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3.5\text{H}_2\text{O}$ offers a significant advantage over
15 other commercially available hydrated zinc borates
since elevated temperatures are required for
compounding many plastics and rubbers. However, some
of the recently developed engineering plastics require
processing at even higher temperatures in the range of
20 about 300-400°C, and it is desirable to have a zinc
borate which has an even higher dehydration
temperature.

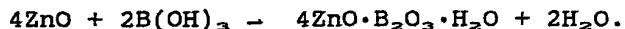
Summary of the Invention

The present invention provides a new crystalline, hydrated zinc borate having a relatively high dehydration temperature which makes it especially useful for use in polymers requiring processing at high temperatures. The anhydrous form of the zinc borate is also provided.

Description of the Invention

The hydrated zinc borate of this invention has the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$. It is a crystalline solid having very slight water solubility and having a dehydration temperature which begins at about 415°C with a rapid loss occurring above 425°C . Such a high dehydration temperature makes this composition especially useful as an additive for polymers requiring high processing temperatures such as the polysulfones, polyamide-imides, polyketones, polyetherketones and polyarylates. The water solubility of the compound is considerably lower than that of other known hydrated zinc borates.

The zinc borate hydrate of this invention can be readily prepared by a variety of methods. The presently preferred method of production comprises the 5 reaction of zinc oxide with a near stoichiometric amount of boric acid (2:1 mole ratio) in water at an elevated temperature, according to the equation



The reaction preferably takes place near the 10 boiling point of the mixture and is promoted by the presence of previously prepared product seed. The concentration of the initial reaction mixture should be greater than about 5% by weight of starting reagents in order to provide a reasonably rapid 15 reaction rate. Preferably, reaction mixtures in the 10-20% by weight range are employed, since they require only a few hours of refluxing in water to go to completion. It is also preferred that a slight molar excess (approximately 5%) of boric acid is used 20 in order to provide complete consumption of zinc oxide in the reaction. The desired hydrated zinc borate product is readily separated from the cooled reaction

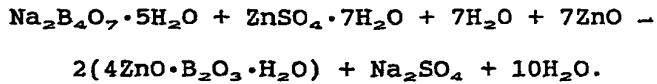
solution by filtration and dried to give the desired crystalline product. It has also been found that more consistent results are obtained when boric acid is added to the zinc oxide in boiling water in at least two separate portions, thereby maintaining the pH of the reaction mixture above about 5.5, and the reaction mixture is efficiently stirred or mixed during the reaction period.

Other methods for preparing the hydrated zinc borate of this invention include hydrolysis of the zinc borate $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ in a refluxing aqueous slurry. It has been found that the concentration of the starting material in the aqueous slurry must be less than about 5% in order to produce a complete reaction. At least five days of continuous reflux at atmospheric pressure of a 5% slurry of starting material is required to give complete hydrolysis. Reflux of the reaction mixture containing free boric acid for an excessive period of time (such as for one month) will convert the zinc borate to the compound $6\text{ZnO}\cdot 5\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ which was previously reported as a product of the hydrothermal reaction of zinc

oxide and boric acid at 165°C. See Lehmann, H.-A. et al., Zeitschrift fur Anorganische und Allgemeine Chemie, 1967, 354, Page 37.

The zinc borate of this invention may also
5 be prepared by reacting $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ with a stoichiometric amount of zinc oxide in refluxing water. This reaction is also facilitated by the presence of seed crystals of previously prepared zinc borate $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In some cases, the reaction
10 appears to be catalyzed by the presence of zinc ion such as supplied by a small amount of zinc chloride or zinc sulfate.

A fourth method for preparing the $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ of this invention is by reaction of
15 sodium tetraborate with a zinc salt such as zinc sulfate and zinc oxide in boiling water, for example, according to the equation



The presence of about 5% seed product facilitates the reaction which goes to completion within a few hours.

Examples

5 The following examples illustrate preparation and use of the zinc borates of this invention.

Example I

200 Grams of $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ (0.460 mol)
10 was added to 4.5 L of deionized (DI) water and boiled under reflux for six days. During this time the pH of the reaction solution gradually decreased from 7.8 to about 4.5. The reaction slurry was then filtered, washed with DI water and air dried to give 92.2 g (97%
15 yield) of product, $4\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot \text{H}_2\text{O}$ having the following analysis:

	<u>Calc.</u>	<u>Found</u>
ZnO	78.79	78.35
B ₂ O ₃	16.84	17.04
H ₂ O	4.36	4.88

5 Since slight variations in analyses can be expected, a typical composition of the hydrated zinc borate of this invention can be defined as
3.9-4.1(ZnO)·0.9-1.1(B₂O₃)·0.8-1.2(H₂O).

10 The XRD pattern for the product, set out below, bears no similarity to any known zinc borate compound. The following is the characteristic X-ray diffraction pattern for the hydrated zinc borate.

	2-THETA/degrees	D/degrees	INTENSITY
5	22.21	3.998	100
	18.78	4.721	94
	28.44	3.133	58
	36.31	2.472	55
	31.64	2.826	39
	21.91	4.053	35
10	37.51	2.396	32
	33.82	2.648	31
	37.27	2.410	23
	32.67	2.739	20
	42.86	2.108	19
15	40.65	2.218	19
	55.68	1.650	17
	48.97	1.858	16
	23.91	3.718	13

A portion of the filtrate was evaporated to dryness to give a crystalline solid which was identified as boric acid by its XRD pattern.

10

Example II

A 5-L flask was charged with 100 grams (0.23 mole) of the zinc borate $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$, 74.9 grams (0.92 mol) of ZnO, 7.2 g. (17 mmol) of previously prepared seed product, and 2.0 L DI water. To this slurry was added 0.5 g of ZnCl_2 (3.7 mmol). The mixture was boiled under reflux for six hours with mechanical stirring.

The reaction was then cooled, filtered, and 10 the product air dried to give 146.4 g (98% yield) of $4\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot \text{H}_2\text{O}$, identified by its XRD pattern.

Example III

A 5-L round bottom flask was charged with 488.4 g. of ZnO (6 mol) and 3.5 L of DI water. This 15 slurry was brought to a boil and 28.0 g. of previously prepared seed (0.07 mol) and 97.4 g of boric acid (1.58 mol) was added. After boiling this mixture under reflux with stirring for 2.5 hours, another portion of boric acid (97.4 g.; 1.58 mol) was added.

11

After refluxing with stirring for another 2.5 hours, the reaction mixture was cooled and filtered. The solid product was washed with DI water and air dried to give 629.2 g (97% yield) of
5 $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$.

Example IV

Sodium tetraborate pentahydrate (45.9 g.; 0.158 mol) was dissolved in 1.0 L of hot DI water in a 5-L flask. To this solution was added 43.1 g of
10 $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ (0.15 mol) dissolved in 250 ml water. A white precipitate formed immediately. This mixture was brought to a boil and ZnO (85.5 g.; 1.05 mol) and 6.2 g of previously prepared seed (15 mmol) were added. The reaction mixture was boiled under reflux
15 for six hours. The reaction was cooled, filtered, washed with water and air dried to give 132.7 g (97% yield) of $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ containing some residual zinc oxide.

Zinc borate 4ZnO·B₂O₃

Zinc borate 4ZnO·B₂O₃ can be prepared by the dehydration of the hydrated zinc borate 4ZnO·B₂O₃·H₂O. The dehydration is readily accomplished by heating the 5 hydrated borate at a temperature above 415°C. for a period of time sufficient to remove essentially all water. Generally heating at a temperature in the range of about 500 to 550°C. for about 3 to 5 hours will produce good yields of the desired 4ZnO·B₂O₃.

10 The anhydrous zinc borate 4ZnO·B₂O₃ is non-hygroscopic and is resistant to rehydration even under high humidity conditions. This offers a significant advantage over many other anhydrous metal borate compounds which are often appreciably hygroscopic.

15

Example V

A 50.0 gram (0.12 mol) sample of the zinc borate hydrate of this invention was heated in a furnace at 500-550°C for about 4 hours. This resulted in a weight loss of 2.2 grams, corresponding to the

loss of 0.12 mol of water.

To test for moisture reabsorption, a sample of the resulting anhydrous zinc borate was placed in an open container in a humidity chamber maintained at 5 90% relative humidity and 90°F for one month. After this time, a sample of this material was subjected to thermogravimetric analysis (TGA). Less than 0.1% weight loss was detected upon slowly heating the material over a period of about 2 hours from room 10 temperature to 700°C., indicating that very little moisture was absorbed during prolonged storage under high humidity conditions. Furthermore, no significant weight loss was found when this material was heated continuously at 400°C.

15 The zinc borate compounds of this invention are useful as fire retardant and smoke suppressant additives for a wide range of organic polymer compositions. The polymer systems include the well-known polymers, rubbers and coatings 20 compositions. Examples of such compositions are polyvinyl chloride (flexible and rigid), nylons,

polyolefins (e.g. polyethylene, polypropylene, and ethylene-propylene elastomers such as EPM and EPOM), chlorinated polyolefins, ethylene vinyl acetate, acrylates and acrylic copolymers, polyurethanes 5 (flexible and rigid), polystyrenes, polybutadiene, polyesters, styrene-butadiene rubbers, acrylonitrile-butadiene-styrene (ABS), polysulfones, silicones, neoprene, fluoroelastomers (e.g. ETFE and FEP), cellulastics, polyphenylene oxide, polyethers, 10 polyether imides, polyetherketones, polyethersulfones, epoxies, polycarbonates, phenolics, polyarylates, polyamides, melamine-formaldehyde and alloys and blends of the above.

The zinc borate is incorporated in the 15 polymer systems at levels of from about 1 to 40 parts by weight of additive per 100 parts of resin (phr). Preferably, about 2 to 20 phr is added for best fire retardancy. The polymer systems may also contain other additives which are conventionally used in such 20 compositions, including antimony oxide, alumina trihydrate, stabilizers, plasticizers, halogenating agents, fillers such as calcium and magnesium

15

carbonates, pigments, etc.

The following examples are illustrative of polymer compositions containing the zinc borates of this invention.

5

Example VI

Flexible polyvinyl chloride compositions were prepared with variable amounts of the zinc borates $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ and $4\text{ZnO}\cdot\text{B}_2\text{O}_3$. The formulations were as follows in which parts are by weight.

10

Table I

		Formulation Nos. (parts by weight)						
		1	2	3	4	5	6	7
15	GEON 30 (PVC)	100	100	100	100	100	100	100
	Dioctylphthalate	50	50	50	50	50	50	50
	Epoxidized Soya Oil	5	5	5	5	5	5	5
20	Stabilizer (Therm-Chek 120)	3	3	3	3	3	3	3
	Alumina Trihydrate	30	30	30	30	30	30	30
	Antimony Oxide	0	1.25	2.5	3.75	5.0	7.5	12.5
25	$4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$	0	1.25	2.5	3.75	5.0	7.5	12.5

		Formulation Nos. (parts by weight)			
		8	9	10	11
5	GEON 30	100	100	100	100
	Dioctylphthalate	50	50	50	50
	Epoxidized Soya Oil	5	5	5	5
10	Stabilizer (Therm-Chek 120)	3	3	3	3
	Alumina Trihydrate	30	30	30	30
	Antimony Oxide	0	2.5	7.5	12.5
	4ZnO·B ₂ O ₃	0	2.5	7.5	12.5

The formulations were pressed into test articles and the
 15 fire retardancy determined by measuring the limiting oxygen index (LOI) according to the procedure of ASTM D 2863. The results are given in Table II.

Table II

	<u>Formulation No.</u>	<u>LOI</u>
5	1	25.6
	2	28.1
	3	30.0
	4	32.5
	5	32.9
	6	35.8
10	7	36.1
	8	25.6
	9	29.8
	10	32.3
	11	33.9

15 Smoke suppressant efficacy was determined by measuring the specific optical density ($D_m(\text{corr})$) of smoke generated by burning test samples using a NBS smoke chamber according to the procedure of ASTM E662. The results are set forth in Table III.

Table III

	<u>Formulation No.</u>	<u>D_m (corr)</u>
5	1	184
	2	157
	5	122
	7	126

Example VII

10 The compounds of this invention are also useful as anti-corrosion additives for polymeric coating compositions. To test the hydrated zinc borate $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$, cold rolled steel test panels coated with an unoptimized medium oil alkyd primer
15 paint containing the borate were subjected to continuous salt spray conditions according to the standard test method ASTM B117. Negative controls, consisting of identical steel panels coated with equivalent paint formulations without the zinc
20 borate, were treated simultaneously under the same conditions. The pigment volume concentrations of the two test paints were maintained at the same

level by adjusting the volume of extender, calcium carbonate, used in the formulations. The test paint formulations are given in Table IV. The test paints were each applied to three replicate
5 degreased, burnished standard cold rolled steel test panels using a standard drawdown bar to provide coatings having a dry film thickness of 2 mils. After drying for one week at room temperature, the panels were scribed with a St. Andrew's cross and placed into a standard salt spray chamber. After 400 hours of continuous salt spray exposure at 95°F, the panels were removed and evaluated for blistering according to the standard method ASTM D714. The paint film was then stripped
10 15 using paint remover and the metal surface was evaluated for rusting according to the standard method ASTM D610. The results of these tests are given in Table V.

Table IV

		<u>Formulation No.</u>	
		<u>I</u>	<u>II</u>
5	Pigment Grind:		
	Aroplaz 1082-M-50 alkyd resin	265.3 *	265.3
	Bentone SD-1	4.6	4.6
	Mineral Spirits	42.4	42.4
	Calcium Carbonate	88.0	159.8
10	Titanium Dioxide	212.1	212.1
	Mica	27.0	27.0
	4ZnO·B ₂ O ₃ ·H ₂ O	100.0	-----
	Grind at high speed for 15 minutes and letdown at slow speed.		
15	Letdown:		
	Aroplaz 1082-M-50	159.1	159.1
	Mineral Spirits	140.1	140.1
	4% Calcium Drier	6.4	6.4
20	6% Cobalt Drier	1.3	1.3
	6% Zirconium Drier	3.8	3.8
	Antiskinning Agent	1.3	1.3

* parts by weight

Table V

	Formulation	Blistering		Rust Grade ³	Undercutting
		Frequency ¹	Size ²		
5	I (Zinc Borate)	F	S8	9	Slight
	II (Control)	MD	S2	3	Considerable

1 ASTM D714 blister frequency: F = Few
 10 MD = Medium
 Dense

2 ASTM D714 rates blister size on a
 15 numeral scale of 0 to 10 in which
 blister size increases from S10 (no
 blisters) to S0 (very large blisters).

3 ASTM D610: rust grade 9 corresponds to
 20 minute rusting (less than 0.03% of the
 surface); rust grade 3 corresponds to
 rusting over approximately one sixth of
 the surface.

25 The very low water solubility of the
 compounds of this invention make them especially
 useful for applications in plastics and coatings
 where very low leaching rates are desirable, such
 as under conditions of submersion in water or
 exposure to weathering.

various changes and modifications of the
invention can be made and, to the extent that such
variations incorporate the spirit of this
invention, they are intended to be included within
the scope of the following claims.
5

Claims:

1. A zinc borate having a ZnO:B₂O₃ ratio of 4:1.

2. A zinc borate according to claim 1
5 having the formula 4ZnO·B₂O₃·H₂O.

3. A zinc borate according to claim 1
which has the formula 4ZnO·B₂O₃ and is essentially
anhydrous.

4. Crystalline hydrated zinc borate
10 which has the formula 4ZnO·B₂O₃·H₂O and the
following characteristic x-ray diffraction pattern:

	2-THETA/degrees	D/degrees	INTENSITY
5	22.21	3.998	100
	18.78	4.721	94
	28.44	3.133	58
	36.31	2.472	55
	31.64	2.826	39
	21.91	4.053	35
10	37.51	2.396	32
	33.82	2.648	31
	37.27	2.410	23
	32.67	2.739	20
	42.86	2.108	19
15	40.65	2.218	19
	55.68	1.650	17
	48.97	1.858	16
	23.91	3.718	13

5. A method of producing a crystalline zinc borate of the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ which
20 comprises reacting zinc oxide or salt thereof with boric acid or salt thereof in water at an elevated temperature for a period of time sufficient to form said crystalline zinc borate $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$.

6. A method according to claim 5 in which said reaction takes place at the boiling temperature of the water.

7. A method of producing a crystalline zinc borate of the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ which comprises reacting zinc oxide with boric acid in a mole ratio of about 2:1 in an aqueous solution at an elevated temperature, thereby forming said crystalline zinc borate, and separating said crystalline zinc borate from said aqueous solution.

8. A method according to claim 7 in which a slight molar excess of boric acid is present and said reaction is in the presence of previously prepared seed crystals of said zinc borate.

9. A method according to claim 7 in which said boric acid is added in at least two portions to said zinc oxide in boiling water, thereby maintaining the pH of the reaction mixture above about 5.5.

10. A method of producing a crystalline zinc borate of the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ which comprises reacting zinc borate of the formula $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3.5\text{H}_2\text{O}$ with zinc oxide in boiling water.

5 11. A method of producing a crystalline zinc borate of the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ which comprises reacting sodium tetraborate with a zinc salt in boiling water.

10 12. A method of producing a crystalline zinc borate of the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ which comprises heating an aqueous slurry of less than about 5% by weight concentration of zinc borate $2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3.5\text{H}_2\text{O}$ at reflux temperature for a period of time sufficient to form said crystalline zinc borate $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$.

15 13. A method of producing essentially anhydrous zinc borate $4\text{ZnO}\cdot\text{B}_2\text{O}_3$ which comprises heating hydrated zinc borate of the formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ at a temperature above 415°C . for a period of time sufficient to remove essentially all

water.

14. A fire-retardant, smoke suppressent,
or coating composition comprising an organic
polymer and a zinc borate as claimed in any one of
5 claims 1 to 4.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 92/09900

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C01B 35/12, C08K 3/38
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C01B, C08K, C09C, C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ZEITSCHRIFT FÜR ANORGANISCHE UND ALLGEMEINE CHEMIE, Volume 354, No 1, 1967, (Leipzig), H-A Lehmann et al, "Über Wasserhaltige Zinkborate" page 37 - page 43 --	1-14
A	SUPPLEMENT TO INORGANIC AND THEORETICAL CHEMISTRY, Volume 5, No a, 1980, (London), Mellor Joseph W, "Zinc Borates" page 572 - page 579 -- -----	1-14

Further documents are listed in the continuation of Box C. See patent family annex.

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31-651, epo nl, Fax: (+31-70) 340-3016	Authorized officer Britt-Marie Lundell